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THE COORDINATION CHEMISTRY OF 2,2'-BIPHENYLENEDITHIOPHOSPHINATE AND DIPHENYLDITHIOPHOSPHINATE WITH U, Np, and Pu.

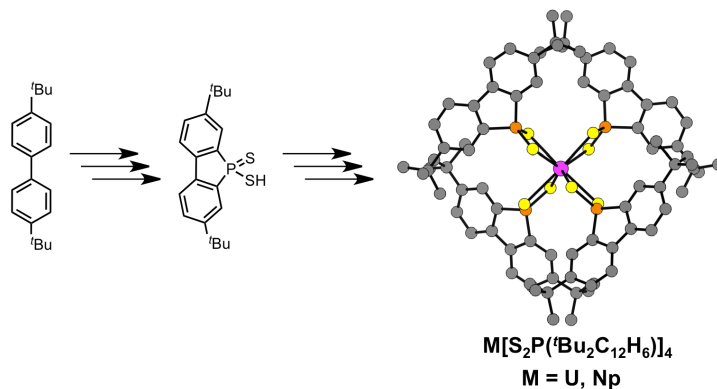
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ABSTRACT

New members in the dithiophosphinic acid family of potential actinide extractants have been prepared: heterocyclic 2,2'-biphenylenedithiophosphinic acids of stoichiometry $HS_2P(R_2C_{12}H_6)$ ($R = H$ or $tert\text{-}Bu$). The time- and atom-efficient syntheses afforded multigram quantities of pure $HS_2P(R_2C_{12}H_6)$ in reasonable yields (~60 %). These

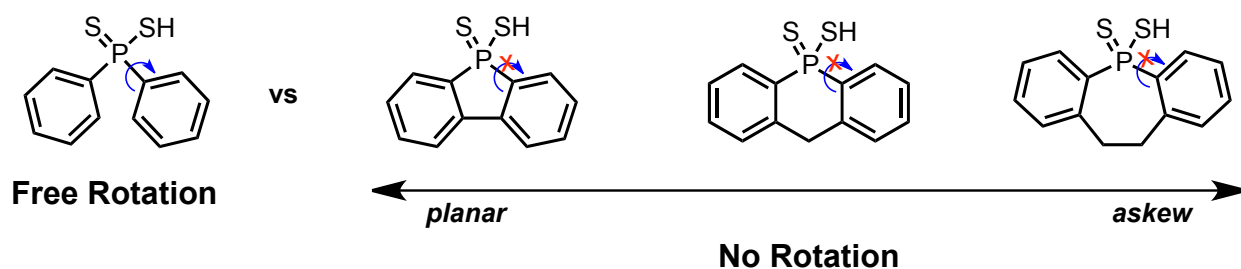
compounds differed from other diaryldithiophosphinic acid extractants in that the aryl rings were bridged by a single C–C linkage that constituted a 5-membered dibenzophosphole ring. These 2,2'-biphenylenedithiophosphinic acids were readily deprotonated to form $\text{S}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)^{1-}$ anions supported by tetraphenylpnictonium cations (ZPh_4^{1+} ; $\text{Z} = \text{P}$ or As). Reactivity comparisons between $[\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]^{1-}$ and $[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]^{1-}$ with U, Np, and Pu showed little influence of the dibenzophosphole ring on actinide coordination chemistry. However, these studies highlighted the relative stability of U^{IV} vs U^{III} , Np^{IV} vs Np^{III} , and Pu^{III} vs Pu^{IV} in the presence of dithiophosphate salts. For instance, reactions involving U^{IV} and Np^{IV} generated $\text{An}[\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]_4$ and $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$. In contrast for Pu^{IV} , reactions with $[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]^{1-}$ provided a mixture of products from which Pu^{III} containing species were observed and the trivalent $\text{Pu}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)]_3(\text{NC}_5\text{H}_5)_2$ reduction product was isolated. Attempts to synthesize analogous trivalent compounds with U^{III} provided the tetravalent $\text{U}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)]_4$ oxidation product. Hence, these results show that, in the presence of dithiophosphate ligands, U^{IV} and Np^{IV} did not spontaneously undergo oxidation or reduction, while Pu^{IV} was readily reduced to Pu^{III} .

INTRODUCTION

There exist considerable interest in solving longstanding problems associated with the indefinite on-site storage of spent fuel at nuclear power plants. Minor actinide (Am, Cm) partitioning and transmutation has emerged as one attractive proposition for achieving this goal.¹⁻⁵ In this approach, after the minor actinides are separated (partitioned) from fission products in the spent

fuel, they are then converted (transmuted) to short-lived isotopes in fast breeder reactors. Partitioning and transmutation is enticing because it recycles the spent fuel and allows additional energy to be harnessed from the nuclear transmutation processes. Unfortunately, there are several technical challenges to the implementation of current partitioning and transmutation strategies on an industrial scale. Perhaps the most daunting *chemical* problem is associated with the partitioning of fissionable minor actinides from the lanthanide fission products. This separation is particularly challenging because – in general – both minor actinides and lanthanides form hard, oxophilic, trivalent ions that share similar chemical and physical properties.⁶⁻⁹

Of the separation strategies proposed previously,^{3,10-17} liquid/liquid extraction tactics relying on dithiophosphinic acids (HS_2PR_2) have emerged as a promising solution to the partitioning problem.^{8,18-25} For example, $\text{HS}_2\text{P}(o\text{-CF}_3\text{C}_6\text{H}_4)_2$ is a unique potential extractant as it gives the largest Am/Eu separation factor reported to date ($\text{SF}_{\text{Am/Eu}} = 100,000$).¹⁹ Although there are many variables that influence the extraction process, it has been proposed that the large separation factors observed for $\text{HS}_2\text{P}(o\text{-CF}_3\text{C}_6\text{H}_4)_2$ may be a consequence of greater covalency in the Am– S_2PR_2 interactions vs. the more ionic Eu– S_2PR_2 interactions.^{18,26} Recent spectroscopic and theoretical studies from a series of $\text{S}_2\text{PR}_2^{1-}$ anions ($\text{R} = \text{Me}, \text{C}_6\text{H}_5, p\text{-CF}_3\text{C}_6\text{H}_4, m\text{-CF}_3\text{C}_6\text{H}_4, o\text{-CF}_3\text{C}_6\text{H}_4, o\text{-MeC}_6\text{H}_4, o\text{-MeOC}_6\text{H}_4$) revealed that Am/Eu separation factors were correlated with the electronic structure of the dithiophosphinate extractant.²⁷ These studies identified that the extent and nature of π -mixing between the aryl groups and the PS_2^{1-} core depended on the orientation of the aryl rings. It was proposed that this geometric configuration provides a unique electronic structure that is poised for selective actinide binding. Hence our recent efforts have focused on further optimizing this entatic state²⁸ for more selective actinide binding by constraining the aryl rings orientations through C–C linkages (Scheme 1).

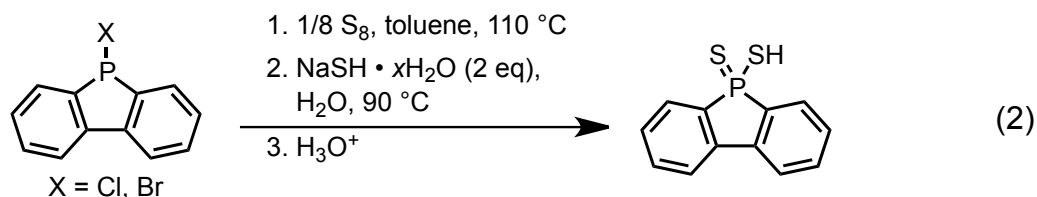
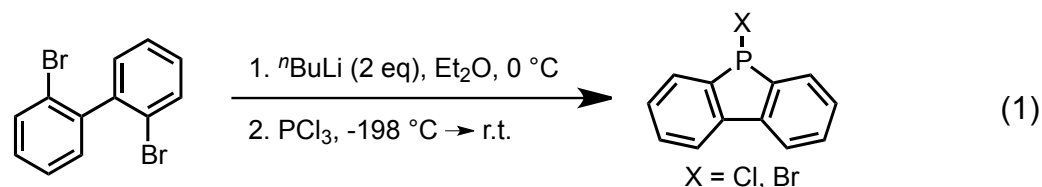


Scheme 1. Tethering of the aryl rings ensures that they are unable to rotate freely about the P–C_{ipso} bond. The size of the central heterocycle can be used to further manipulate orbital mixing between the aryl groups and the PS₂¹⁻ core

Reported herein is the first in a series of synthetic studies describing the preparation of heterocyclic dithiophosphinic acids with tethered aryl groups – specifically, those that contain the 5-membered dibenzophosphole ring. These efforts included preparation of the 2,2'-biphenylenedithiophosphinic acids, HS₂P(R₂C₁₂H₆) (R = H or ^tBu), and their conjugate bases, S₂P(R₂C₁₂H₆)¹⁻, which were isolated as the corresponding tetraphenylpnictonium salts (ZPh₄¹⁺; Z = P or As). Additionally, the coordination chemistry of the 2,2'-biphenylenedithiophosphate anions with uranium, neptunium, and plutonium has been explored in comparison to that of the untethered diphenyldithiophosphate ion, S₂P(C₆H₅)₂¹⁻. These reactivity studies provided a useful platform for evaluating how actinide coordination chemistry with dithiophosphinates was (or was not) affected by the tethering of the aryl rings. Moreover, they highlighted the different electron transfer reactions available to uranium, neptunium, and plutonium in the presence of dithiophosphate salts.

RESULTS AND DISCUSSION

SYNTHESES OF $\text{HS}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)$ ($\text{R} = \text{H}$, $t\text{Bu}$). The 2,2'-biphenylenedithiophosphinic acid, $\text{HS}_2\text{P}(\text{C}_{12}\text{H}_8)$, was prepared as described in Eq 1 and 2.



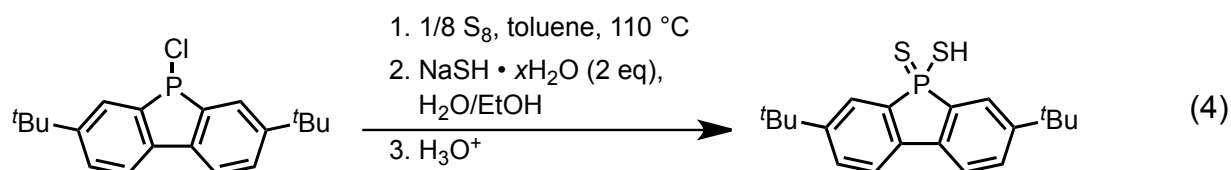
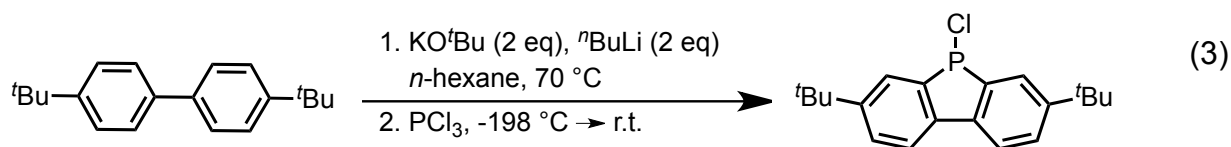
The synthetic procedure began with treating the commercially available 2,2'-dibromobiphenyl, $\text{Br}_2\text{C}_{12}\text{H}_8$, with two equivalents of *n*-butyllithium to generate the known 2,2'-dilithiobiphenyl compound, $\text{Li}_2(\text{C}_{12}\text{H}_8)$.²⁹ This organolithium reagent has been reported to react with phosphorus trichloride to generate 5-chloro-5*H*-dibenzo[*b,d*]phosphole in good yield.²⁹ In our hands, this reaction afforded a second product that was characterized by ^{31}P NMR spectroscopy as the 5-bromo-5*H*-dibenzo[*b,d*]phosphole, such that the chloro- to bromophosphole ratio was approximately 3:2 (Eq 1). This interpretation was supported by similar halogen exchange reactions noted in the preparation of some closely related compounds.¹⁹ It was not necessary to separate the 5-chloro-5*H*-phosphole from the 5-bromo-5*H*-phosphole, as both halophosphines behaved similarly in successive conversion to the dithiophosphinic acid.

The usual method to prepare dithiophosphinic acids from halophosphines involves reduction to the corresponding phosphine and subsequent treatment with elemental sulfur followed by addition of either ammonium carbonate or ammonium hydroxide.^{19,21,27,30} Unfortunately, in our

laboratories this methodology failed when applied to the dibenzo[*b,d*]phosphole derivatives, and intractable mixtures formed instead. We found, however, that addition of elemental sulfur directly to the halophosphine followed by addition of sodium hydrosulfide hydrate (NaSH•*x*H₂O) and aqueous workup cleanly provided the desired 2,2'-biphenylenedithiophosphinic acid, HS₂P(C₁₂H₈), in 54% overall yield from Br₂C₁₂H₈ via what is presumed to be the thiophosphinyl halide.

This ‘one-pot’ sulfurization method had several advantages over prior approaches. The purification protocol was simple and avoided issues resulting from the instability of dithiophosphinic acids toward hydrolysis or thermolytic conversion (with loss of H₂S) to the corresponding anhydrosulfide. Undesired reaction byproducts and unreacted starting materials were also easily removed by distillation in vacuum, filtration, or washing with hexane. Moreover, this atom-efficient method avoided additional reduction steps, could be carried out in approximately one day, and proceeded in good yields on multi-gram scales.

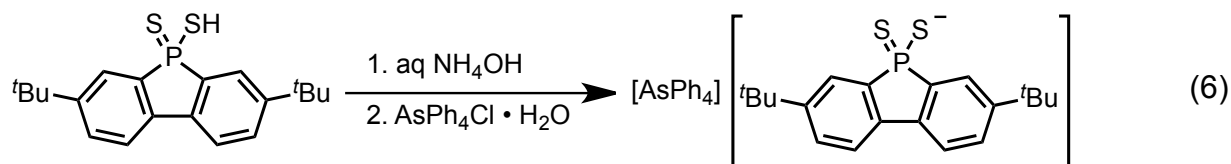
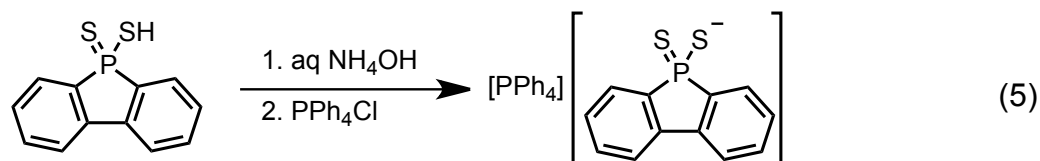
Similar methodology was used to prepare the di-*tert*-butyl substituted derivative, 4,4'-di-*tert*-butyl-2,2'-biphenylenedithiophosphinic acid, HS₂P(*t*Bu₂C₁₂H₆), as illustrated in Eq. 3 and 4.



The synthesis relied on previous work that had established 4,4'-di-*tert*-butylbiphenyl, ${}^t\text{Bu}_2\text{C}_{12}\text{H}_8$, could be deprotonated at the 2 and 2' positions with Schlosser's base, ${}^n\text{BuLi/KO}^t\text{Bu}$.³¹ We found that the *in situ* generated organometallic dianion reacted smoothly with phosphorus trichloride to afford 3,7-di-*tert*-butyl-5-chloro-5*H*-dibenzo[*b,d*]phosphole, $\text{ClP}({}^t\text{Bu}_2\text{C}_{12}\text{H}_6)$. Treatment of the chlorophosphole with elemental sulfur and sodium hydrosulfide hydrate (as discussed above) afforded the 4,4'-di-*tert*-butyl-2,2'-biphenylenedithiophosphinic acid, $\text{HS}_2\text{P}({}^t\text{Bu}_2\text{C}_{12}\text{H}_6)$, cleanly in 52% overall yield from the commercially available ${}^t\text{Bu}_2\text{C}_{12}\text{H}_8$ hydrocarbon starting material.

Although the synthetic method that provided $\text{HS}_2\text{P}({}^t\text{Bu}_2\text{C}_{12}\text{H}_6)$ was similar to the $\text{HS}_2\text{P}(\text{C}_{12}\text{H}_8)$ analogue, the ${}^t\text{Bu}$ substituents in $\text{HS}_2\text{P}({}^t\text{Bu}_2\text{C}_{12}\text{H}_6)$ provided increased organic phase solubility. For example, our qualitative observations suggested that the unsubstituted $\text{HS}_2\text{P}(\text{C}_{12}\text{H}_8)$ acid is only mildly (< 20 mg/mL) soluble in chloroform and dichloromethane, and essentially insoluble in toluene, tetrahydrofuran, diethyl ether, *n*-hexane, and acetonitrile after isolation as a microcrystalline solid. In contrast, aside from hexane, the substituted $\text{HS}_2\text{P}({}^t\text{Bu}_2\text{C}_{12}\text{H}_6)$ analogue readily dissolved in all of the aforementioned solvents. Based on these results, we anticipate that the limited solubility of $\text{HS}_2\text{P}(\text{C}_{12}\text{H}_8)$ will inhibit its use as a ligand and as an extractant in comparison to the more soluble $\text{HS}_2\text{P}({}^t\text{Bu}_2\text{C}_{12}\text{H}_6)$ analogue.

SYNTHESES AND STRUCTURES OF $[\text{ZPh}_4][\text{S}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)]$ ($\text{R} = \text{H}, {}^t\text{Bu}$; $\text{Z} = \text{As}, \text{P}$). The $\text{HS}_2\text{P}(\text{C}_{12}\text{H}_8)$ and $\text{HS}_2\text{P}({}^t\text{Bu}_2\text{C}_{12}\text{H}_6)$ acids were readily deprotonated with mild base in air as shown in Eq. 5 and 6. For example, treatment of the dithiophosphinic acids with aqueous NH_4OH followed by addition of tetraphenylpnictonium chloride (ZPh_4 , $\text{Z} = \text{P}$ or As) provided the $[\text{ZPh}_4][\text{S}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)]$ salts in reasonable crystalline yields ranging from 41 to 45%.



Single crystals of $[\text{PPh}_4][\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)]$ and $[\text{AsPh}_4][\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]$ that were suitable for X-ray diffraction studies were grown by slow evaporation of acetone/water solutions. We note that single crystals of $[\text{PPh}_4][\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]$ were also obtained, but disorder associated with the $\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)^{1-}$ anions prohibited the generation of a meaningful model of the data. The structural metrics for $[\text{PPh}_4][\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)]$ and $[\text{AsPh}_4][\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]$ were similar, as evident from the molecular structures shown in Figures 1 and 2 and the selected bond distances and angles summarized in Tables 1 and 2. In each anion, the S–P bond distances were equal within error. These distances and the S–P–S angles were similar to those observed previously in other $\text{S}_2\text{PR}_2^{1-}$ salts (Table 2). The solid-state data confirmed that the dithiophosphinic acids contained a planar dibenzophosphole unit. The C–C distances for the linkage between the two aromatic rings were 1.468(4) and 1.476(3) Å in $\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)^{1-}$ and $\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)^{1-}$, respectively. These values were consistent with the presence of a $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$ single bond. For comparison, the analogous $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$ single bond length in fluorene is 1.472(3) Å.³²

In both $[\text{PPh}_4][\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)]$ and $[\text{AsPh}_4][\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]$, the central phosphorus atoms were almost exactly in the plane defined by the biphenylene carbon atoms, with deviations of 0.002 and 0.048 Å, respectively. Although the geometric constraints imposed by the 5-membered

dibenzophosphole ring systems in $S_2P(R_2C_{12}H_6)^{1-}$ decreased the C–P–C angle ($\sim 90^\circ$) by approximately 10° in comparison to the unconstrained $S_2P(C_6H_5)_2^{1-}$ anion, which had an analogous angle of $103.5(1)^\circ$ (Table 2),²⁷ the S–P–S angles were largely unaffected by this structural change. For example, the $118.53(4)$ and $119.21(3)^\circ$ angles in $S_2P(C_{12}H_8)^{1-}$ and $S_2P(tBu_2C_{12}H_6)^{1-}$ were essentially equivalent to those observed in other $S_2PR_2^{1-}$ anions (Table 2). When the rotameric conformations of the tBu substituents were neglected, the $S_2P(R_2C_{12}H_6)^{1-}$ anions had nearly ideal C_{2v} symmetry.

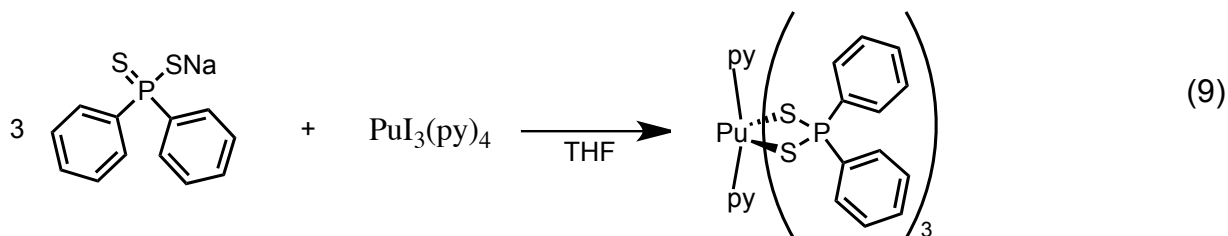
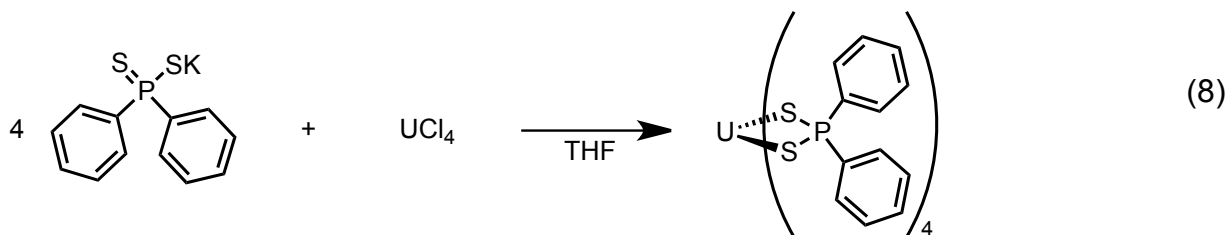
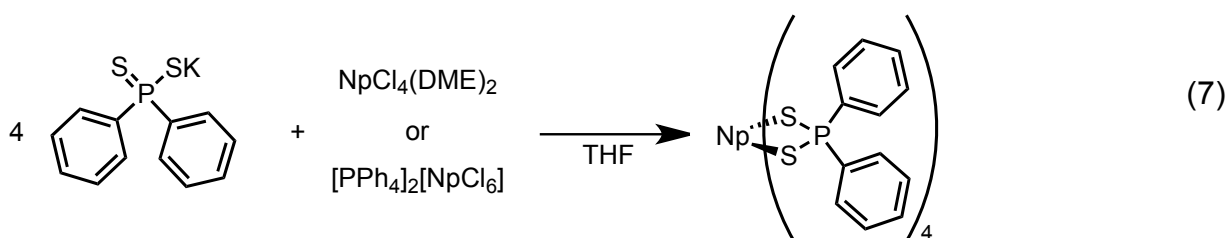
NMR ANALYSIS FROM $HS_2P(R_2C_{12}H_6)$ ($R = H, tBu$) vs. $[ZPh_4][S_2P(R_2C_{12}H_6)]$ ($R = H, tBu$; $Z = As, P$). Two aspects of the ^{31}P NMR chemical shifts of the new dithiophosphinic acids were notable. The first observation indicated that, in chloroform, the two biphenylenedithiophosphinic acids had ^{31}P NMR chemical shifts near 46 ppm, whereas the untethered $HS_2P(C_6H_5)_2$ analogue had a ^{31}P NMR chemical shift of 56 ppm. This comparison suggested that the tethering of the two aryl rings shielded the ^{31}P nucleus by 10 ppm. The second notable observation showed that the change in chemical shift between the free tethered acid $HS_2P(R_2C_{12}H_6)$ in chloroform and the tethered conjugate base $S_2P(R_2C_{12}H_6)^{1-}$ in acetonitrile was 15 ppm. In contrast, the untethered chemical shift difference from the diaryldithiophosphinic acids and conjugate bases, $HS_2PR_2/S_2PR_2^{1-}$, were much smaller, only 5 to 9 ppm (Figure 3).²⁷ Both of these differences might reflect changes in the electronic structure that result from the coplanarity of the aryl rings and the phosphorus atom. As such, efforts are underway to investigate the impact of such aryl ring coplanarity on orbital mixing between the aryl groups and the PS_2^{1-} core using P and S K-edge X-ray absorption spectroscopy and density functional theory calculations.

SYNTHESES AND STRUCTURE OF ACTINIDE DITHIOPHOSPHINATES. To evaluate the impact of tethered the aryl rings on dithiophosphate coordination chemistry with actinide elements, it was important to have first characterized the reactivity with the corresponding untethered diaryldithiophosphate. However, few such actinide compounds have been previously isolated. To the best of our knowledge, besides some uranyl species,³³ only $\text{Th}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$,^{34,35} $\text{Th}[\text{S}_2\text{P}(p\text{-MeOC}_6\text{H}_5)_2]_4$,³⁶ and $\text{U}[\text{S}_2\text{P}(p\text{-MeOC}_6\text{H}_5)_2]_4$ ³⁶ compounds had been described alongside a few actinide diaryldiselenophosphinates.³⁷ Accordingly, we turned our efforts toward the investigation of uranium, neptunium, and plutonium complexation by the diphenyldithiophosphate anion, $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$ before exploring the actinide reactivity of 2,2'-biphenylenephosphinate, $\text{S}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)^{1-}$.

The homoleptic coordination complexes tetrakis(diphenyldithiophosphinato)uranium(IV) and -neptunium(IV) were prepared as shown in Eq. 7 and 8 by methods analogous to those used for $\text{Ln}(\text{S}_2\text{PR}_2)_4^{1-}$,^{38,39} $\text{An}(\text{S}_2\text{PR}_2)_4$,^{34,36} and $\text{M}(\text{Se}_2\text{PR}_2)_4$ ^{36,37} species. Thus, potassium diphenyldithiophosphate (prepared by deprotonation of the dithiophosphinic acid with potassium hexamethyldisilazide in toluene) reacted with UCl_4 to afford green needles of $\text{U}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ and with $[\text{PPh}_4]_2[\text{NpCl}_6]$ or $\text{NpCl}_4(\text{DME})_2$ to afford red blocks of $\text{Np}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$. Crystals suitable for X-ray diffraction studies were obtained by vapor diffusion of Et_2O into concentrated THF solutions. Additionally, these uranium and neptunium compounds were characterized by UV-vis, ^1H NMR, and ^{31}P NMR (See Experimental and Supporting Information). While the uranium compounds were also characterized by IR-spectroscopy and elemental analysis, radiological hazards associated with the neptunium compounds prohibited use of these techniques. The uranium compound could also be prepared from trivalent uranium

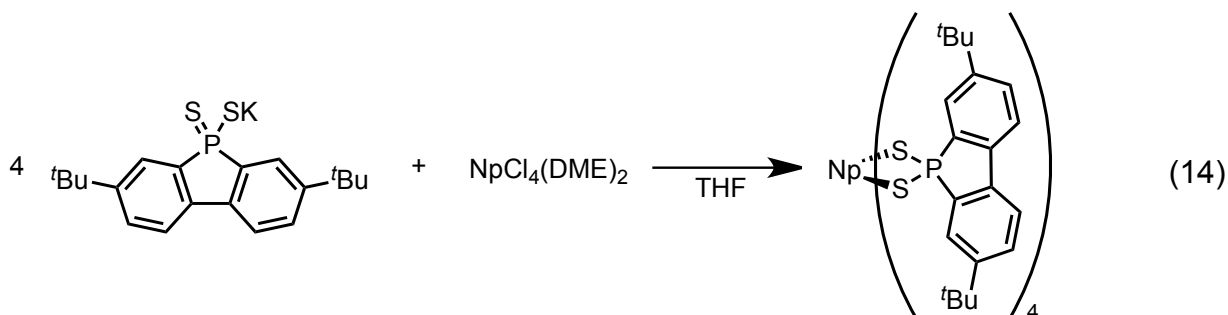
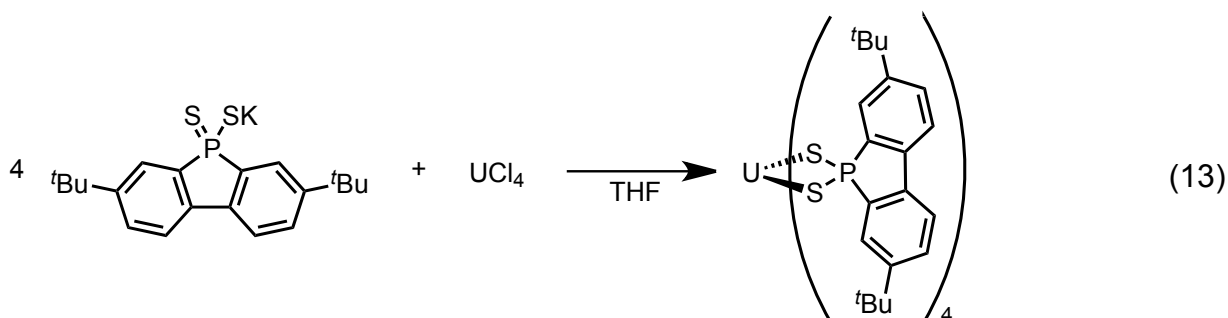
starting materials. Thus, treatment of $\text{U}[\text{N}(\text{SiMe}_3)_2]_3$ with $\text{HS}_2\text{P}(\text{C}_6\text{H}_5)_2$ afforded the tetravalent $\text{U}^{\text{IV}}[(\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2)_4]$ oxidation product in modest yield (64%). Unfortunately, the identity of the reduced partner in this redox reaction was not elucidated.

Our attempts to synthesize the Pu^{IV} analogue by similar means were unsuccessful. Instead, a mixture of products was isolated that contained Pu^{III} species, as judged by the observed UV-vis spectra. However, by treating the trivalent plutonium complex $\text{PuI}_3(\text{NC}_5\text{H}_5)_4$ ^{40,41} with $\text{KS}_2\text{P}(\text{C}_6\text{H}_5)_2$, a few crystals of the the neutral bis(pyridine) adduct $\text{Pu}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3(\text{NC}_5\text{H}_5)_2$ were obtained (Eq. 9).



Using insight derived from the reactivity discussed above, actinide coordination chemistry with the new 2,2'-biphenylenephosphinate anions was similarly investigated. Owing to the

relatively poor solubility of $\text{HS}_2\text{P}(\text{C}_{12}\text{H}_8)$ in organic solvents, we chose to focus our efforts on exploring the reactivity of only the *tert*-butyl derivative $\text{HS}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)$. Additionally, given the complex redox behavior observed for Pu^{IV} with $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$, reactions between plutonium and the $\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)^{1-}$ were not pursued. Thus, the reaction of UCl_4 or $\text{NpCl}_4(\text{DME})_2$ with potassium 4,4'-di-*tert*-butyl-2,2'-biphenylenedithiophosphate, $\text{KS}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)$, in THF afforded the homoleptic compounds $\text{An}[\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]_4$ where $\text{An} = \text{U}$ or Np , in yields of 76% and 49%, respectively (Eq. 13 and 14). Green prisms of $\text{U}[\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]_4$ were grown from toluene/THF/hexane and dark red prisms of $\text{Np}[\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]_4$ were obtained from toluene/ Et_2O /hexane.



STRUCTURAL COMPARISONS OF $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ AND $\text{An}[\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)_2]_4$. The molecular structures from $\text{Np}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$, $\text{Pu}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3(\text{NC}_5\text{H}_5)_2$ and $\text{Np}[\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]_4$

have been provided in Figures 4-6 while molecular structures from $\text{U}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ and $\text{U}[\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]_4$ were included in the Supporting Information. The $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ complexes were isomorphous with one another. Similarly, the $\text{An}[\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]_4$ compounds adopted very similar molecular structures, although they crystallized in different space groups (Table 3). Selected distances and angles for all five compounds were summarized in Table 4.

In each of the $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ and $\text{An}[\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]_4$ compounds, the eight sulfur atoms of the four bidentate dithiophosphinate ligands adopted a distorted D_{2d} trigonal dodecahedron about the actinide center (Figure 7). Hence, the phosphorus atoms were arranged in the second shell as a flattened tetrahedron. Similarly, for $\text{Pu}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3(\text{NC}_5\text{H}_5)_2$, the six sulfur and two nitrogen atoms attached to the plutonium center were best described as forming a distorted trigonal dodecahedron around the central Pu^{3+} ion. With this designation, the pyridine ligands occupied the “outer” sites of one of the two interpenetrating trapezoids.

The metric parameters internal to the $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$ ligand in the U, Np, and Pu complexes were essentially identical (Table 4). Thus, all of the P–S distances were ~ 2.01 Å, the P–C distances were ~ 1.81 Å, and the C–C_{aryl} distances were ~ 1.38 Å. Similarly, the S–P–S angles were $\sim 110^\circ$ and the C–P–C angles were $\sim 105^\circ$. As expected, the An–S distances depended on the identity of the actinide ion with the average values of 2.85 ± 0.03 , 2.82 ± 0.03 , and 2.93 ± 0.02 Å for U^{IV} , Np^{IV} , and Pu^{III} , respectively; exactly tracking the actinide ionic radius. For similar reasons, the measured S–M–S angles of $70.6^\circ \pm 0.2$ and $70.8^\circ \pm 0.1$ for U^{IV} and Np^{IV} were slightly smaller ($68.7^\circ \pm 0.6$) for the larger Pu^{III} ion.

The distances and angles in the $\text{An}[\text{S}_2\text{P}(\text{Bu}_2\text{C}_{12}\text{H}_6)]_4$ complexes were very similar to those observed from the $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_x$ complexes (Table 4). For example, the P–S and P–C distances were again ~ 2.01 and ~ 1.80 Å, and the S–P–S and S–M–S angles are $\sim 109^\circ$ and $\sim 70^\circ$. The

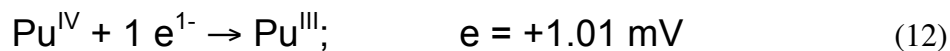
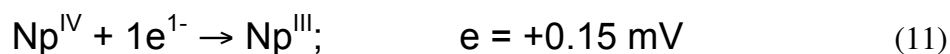
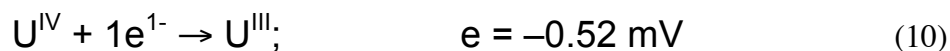
average An–S distance of 2.85 ± 0.02 for U and 2.83 ± 0.01 Å for Np were also essentially identical with those seen in their $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$ analogs. The major difference between the $\text{An}[\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]_4$ and $\text{An}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)]_x$ structures was the C–P–C angle. For example, instead of the $\sim 105^\circ$ value seen for the $\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2^{1-}$ complexes, this angle was reduced to $\sim 92^\circ$ in the $\text{An}[\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]_4$ complexes. These observations can be rationalized by the geometric constraints imposed by the 5-membered PC_4 ring.

CONCLUDING REMARKS

We have described the synthesis of the first 2,2'-biphenylenedithiophosphinic acids, $\text{HS}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)$, where $\text{R} = \text{H}$ or tBu . These new compounds were prepared in multigram quantities, in moderate yield, and in high purity by what was essentially a ‘one-pot’ procedure. Briefly, the four step synthetic method could be summarized by (1st) generation of a biaryl-dianion, (2nd) addition of phosphorous trichloride to form a 5-halo-5*H*-dibenzo[*b,d*]phosphole, (3rd) oxidation of the phosphorous atom with elemental sulfur to provide a thiophosphinyl halide, and (4th) nucleophilic addition of sodium hydrosulfide followed by acidification to afford $\text{HS}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)$. These dithiophosphinic acids were readily deprotonated to the corresponding $\text{S}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)^{1-}$ anions, which were isolated as salts with tetraphenylpnictonium organic cations. In this respect, these salts represent prime candidates for electronic structure studies (currently underway). For instance, the bulky cations guard against bridging interactions, ensuring that that the P–S bond within the highly symmetric $\text{S}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)^{1-}$ anions can be discretely probed spectroscopically. These air and moisture stable salts were also identified as chemical relatives of the well-known class of untethered diaryldithiophosphinates, some of which are able to extract actinides from lanthanide/actinide mixtures. The biphenylenedithiophosphinates differ from

other aryldithiophosphinates in that their aryl rings are tied together by means of a C–C single bond to form a planar 5-membered PC₄ phosphole ring.

We have also prepared the five new actinide dithiophosphate complexes U[S₂P(^tBu₂C₁₂H₆)]₄, Np[S₂P(^tBu₂C₁₂H₆)]₄, U[S₂P(C₆H₅)₂]₄, Np[S₂P(C₆H₅)₂]₄ and Pu[S₂P(C₆H₅)₂]₃(NC₅H₅)₂. These new compounds were fully characterized and their structures determined using X-ray crystallography. Attempts to prepare the plutonium analogue using S₂P(C₆H₅)₂¹⁻ produced a mixture of products from which the trivalent plutonium reduction products Pu[S₂P(C₆H₅)₂](NC₅H₅)₂ was isolated as single crystals. In contrast, in the presence of diphenyldithiophosphate, uranium and neptunium preferred the tetravalent oxidation state. These observations were consistent with reduction potentials reported in the literature for these elements (Eq 10-12),^{40,42}



While the generality of these electron transfer reactions have yet to be established – especially in air and acidic media – these results provocatively suggest that the Pu^{III} oxidation state should be considered in other systems when in the presence of dithiophosphate extractants.

The structural metrics of the actinide dithiophosphate complexes suggested that the rotational constraints imposed by the dibenzo[*b,d*]phosphole ring system in S₂P(^tBu₂C₁₂H₆)¹⁻ had few structural consequences in comparison to the untethered S₂P(C₆H₅)₂¹⁻ ligands, except the expected closing of the C–P–C angle. The electronic effects, however, may be more significant.

This seems especially plausible in view of our recent experimental and theoretical results, which indicated that the polarizability of diaryldithiophosphinates and their ability to discriminate between lanthanides and actinides is strongly influenced by subtle changes in the relative orientation of the aryl rings.^{43,44} Hence, our current efforts are focused on characterizing the ability of the biphenylenedithiophosphinates, $\text{HS}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)$, to separate the minor actinides (Am, Cm) from the early lanthanides (Nd, Eu). Moreover, we are hopeful that the synthetic methodology described herein will be useful in the design and synthesis of improved extractants relevant to the development of advanced nuclear fuel cycles.

EXPERIMENTAL SECTION

General Experimental Considerations. ■ **Caution!** The ^{238}U isotope is a low specific-activity (primarily) α -particle emitting radionuclide that decays to α -, β -, and γ -emitting isotopes. Its use presents hazards to human health. The ^{237}Np and ^{239}Pu isotopes are high specific-activity radionuclides and their use presents relatively higher hazards to human health. This research was conducted in a radiological facility with appropriate analyses of these hazards and implementation of controls for the safe handling and manipulation of these toxic and radioactive materials.

The starting materials UCl_4 ,⁴⁵ $\text{PuI}_3(\text{py})_4$,⁴⁰ $[\text{PPh}_4]_2[\text{NpCl}_6]$,⁴⁶ $\text{NpCl}_4(\text{DME})_2$,⁴⁷ and $\text{U}[\text{N}(\text{SiMe}_3)_2]_3$ ⁴⁰ were prepared by means of literature procedures. UCl_4 was obtained from laboratory stocks. All other reagents were obtained from Aldrich, with the exception of elemental sulfur and tetraphenylarsonium chloride hydrate (Acros), and were used as received. Toluene, diethyl ether, and *n*-hexane were dried by vacuum distillation from sodium/benzophenone, and degassed by three freeze-pump-thaw cycles before use. All reactions

involving Pu and Np were performed inside an MBraun Labmaster 130 glovebox filled with an ultra-high purity helium gas atmosphere, and operated at negative pressure relative to the laboratory atmosphere, using solvents (Aldrich) that were dried over 3 or 4 Å molecular sieves. All other reactions were performed under argon using standard Schlenk techniques with rigorous exclusion of air and moisture unless explicitly stated otherwise. All H₂O used during synthetic manipulations was purified to 18.2 MΩ/cm resistivity using a Thermo-Scientific Barnstead Nanopure or Millipore Nanopure water purification system. Deuterated solvents were used as received or stored over were dried over 3 or 4 Å molecular sieves for several days before use. Elemental analyses were carried out by the Micro-Mass facility at the University of California, Berkeley, and by the School of Chemical Sciences Microanalytical Laboratory at the University of Illinois, Urbana-Champaign. The infrared spectra were recorded on a Nicolet Magna-IR System 750 spectrometer or a Nicolet IR200 FTIR spectrometer as Nujol mulls between KBr plates. The ¹H and ³¹P NMR spectra were obtained on a Bruker Avance 300 MHz, Bruker Avance 400 MHz, or Varian VXR 500 MHz NMR spectrometer at ambient temperature; radioactive samples were placed inside 5 mm NMR tubes equipped with 4 mm PTFE tube liners. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to TMS (¹H) or H₃PO₄ (³¹P). High-resolution mass spectra were collected by the School of Chemical Sciences Mass Spectrometry Laboratory at the University of Illinois. Electronic absorption spectra were recorded on a Varian Cary 6000i UV/vis/NIR spectrophotometer.

Mixture of 5-chloro-5H-dibenzophosphole and 5-bromo-5H-dibenzophosphole, XP(C₁₂H₈) (X = Br, Cl). This procedure is a modification of a literature recipe.²⁹ A solution of 2,2'-dibromobiphenyl (2.49 g, 7.98 mmol) in Et₂O (50 mL) was cooled to 0 °C and treated

dropwise with $n\text{BuLi}$ (10.0 mL of a 1.6 M solution in hexanes, 16.0 mmol). The resulting light yellow solution was stirred at 25 °C for 1 h and then cooled to 196 °C with liquid N_2 . Phosphorus trichloride (5.0 mL, 57.2 mmol) was then added dropwise on top of the frozen mixture. The flask was allowed to warm to 25 °C, and vigorous stirring was commenced as soon as possible. A white precipitate formed, and the mixture was stirred at 25 °C for an additional 15 min. Volatile material (including the excess PCl_3) was removed under reduced pressure, and the residue was subsequently kept under vacuum at 35 °C for 1 h. The resulting mixture of $\text{BrP}(\text{C}_{12}\text{H}_8)$ and $\text{ClP}(\text{C}_{12}\text{H}_8)$ was separated from a light yellow solid by extraction into toluene (2 \times 15 mL); the extracts were filtered and combined. The resulting mixture of 5-halo-5H-dibenzophospholes in toluene was used in subsequent reactions without further purification. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, toluene): δ 68.2 (s, ClPR_2), 49.3 (s, BrPR_2). Lit:²⁹ δ 69.0 (s, ClPR_2). The ratio of $\text{BrP}(\text{C}_{12}\text{H}_8)$ to $\text{ClP}(\text{C}_{12}\text{H}_8)$ was *ca.* 2:3 as judged from integration of the ^{31}P NMR spectrum.

2,2'-Biphenylenedithiophosphinic acid, $\text{HS}_2\text{P}(\text{C}_{12}\text{H}_8)$. To the above mixture of 5-chloro-5H-dibenzophosphole and 5-bromo-5H-dibenzophosphole (theoretical yield: 7.98 mmol) in toluene (30 mL) was added elemental sulfur (256 mg, 0.998 mmol reckoned as S_8). After the mixture had been heated to reflux for 16 h, the light yellow solution was cooled to 25 °C and solvent was removed in vacuum. The flask was opened to air and the yellow solid was suspended in a solution of sodium hydrosulfide hydrate (1.47 g, *ca.* 15.9 mmol NaSH) in water (75 mL). The flask was equipped with a reflux condenser that was vented with a cannula to a 2.5 M aq. NaOH solution (to sequester evolved H_2S). The flask was purged with argon, and the mixture was heated to 90 °C for 1 h, during which time most of the solids dissolved. The mixture was

allowed to cool to 25 °C and then was filtered open to air using a vacuum filtration apparatus to remove a small amount of tan precipitate. The filtrate was acidified with 2.4 M aqueous HCl (35 mL). The resulting solution was extracted with CH₂Cl₂ (3 × 25 mL), and the organic extracts were separated from the aqueous solution, combined, and taken to dryness to afford the product as a light beige powder. Crude yield: 1.15 g (58% from 2,2'-dibromobiphenyl). Further purification was carried out by dissolving the HS₂P(C₁₂H₈) in MeCN (75 mL) and allowing the solution to evaporate to approximately 20 mL. This procedure provided HS₂P(C₁₂H₈) as pale yellow plates. Crystalline yield: 1.07 g (54% from 2,2'-dibromobiphenyl). ¹H NMR (400 MHz, CDCl₃): δ 7.98 (dddd, *J* = 12.2, 7.5, 1.3, 0.7 Hz, 2H, 3,3'-CH), 7.79 (dddd, *J* = 7.7, 3.6, 1.1, 0.7 Hz, 2H, 6,6'-CH), 7.60 (dddd, *J* = 7.7, 7.5, 1.9, 1.3 Hz, 2H, 5,5'-CH), 7.51 (dddd, *J* = 7.5, 7.5, 4.3, 1.1 Hz, 2H, 4,4'-CH). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ 46.9 (s). HRMS *m/z* (EI⁺). Calcd: 247.9883 [M⁺]; found: 247.9883. IR (cm⁻¹): 3066 m, 2959 s, 2925 s, 2854 s, 2330 br m, 1592 w, 1470 m, 1439 s, 1377 w, 1269 w, 1157 w, 1128 m, 1066 m, 966 w, 841 w, 756 s, 722 s, 658 s, 617 w, 541 m, 520 w, 483 w, 449 m, 413 m.

Tetraphenylphosphonium 2,2'-Biphenylenedithiophosphinate, [PPh₄][S₂P(C₁₂H₈)]. A solution of HS₂P(C₁₂H₈) (50.0 mg, 0.201 mmol) in aqueous NH₄OH (15 mL of a 3.6 M solution, 0.540 mmol) was treated dropwise in air with a solution of tetraphenylphosphonium chloride (120 mg, 0.320 mmol) in water (5 mL). A white precipitate formed immediately. After the mixture had been stirred at 25 °C for 5 min, the precipitate was collected by vacuum filtration and the solid was washed with H₂O (3 × 5 mL). The solid was dissolved in a 1:1 mixture of acetone (5 mL) and H₂O (5 mL) and the resulting solution was allowed to evaporate slowly in air to approximately 2 mL. The product was isolated as pale yellow needles. Yield: 48.1 mg (41%).

Anal. Calcd. for $C_{36}H_{28}P_2S_2$: C, 73.7; H, 4.81; P, 10.56; S, 10.93. Found: C, 73.5; H, 4.67; P, 10.46; S, 10.80%. 1H NMR (500 MHz, d_3 -MeCN): δ 7.94-7.88 (m, 4H, Ar-H), 7.77-7.63 (m, 20H, Ar-H), 7.36 (dddd, $J = 7.3, 7.2, 1.6, 1.4$ Hz, 2H, 5,5'-CH), 7.33 (dddd, $J = 7.2, 7.2, 3.4, 1.3$ Hz, 2H, 4,4'-CH). $^{31}P\{^1H\}$ NMR (162 MHz, d_3 -MeCN): δ 61.1 (s, $S_2PR_2^-$), 24.4 (s, PPh_4^+). IR (cm^{-1}): 3408 br, 3057 w, 2924 s, 2855 s, 1585 w, 1463 m, 1438 m, 1377 w, 1316 w, 1261 w, 1162 w, 1107 m, 1026 w, 998 w, 759 m, 724 s, 692 m, 656 s.

3,7-Di-*tert*-butyl-5-chloro-5H-dibenzo[*b,d*]phosphole, $ClP(tBu)_2C_{12}H_6$. To 4,4'-di-*tert*-butylbiphenyl (10.65 g, 40.0 mmol) in hexane (75 mL) was added $nBuLi$ (50 mL of a 1.6 M solution in hexanes, 80.0 mmol). To the mixture was added KO^tBu (9.78 g, 80.0 mmol) in one portion against a counterflow of argon. The resulting bright magenta mixture was brought to reflux for 20 h, during which time the solution color became deep purple. The solution was cooled to $-196^\circ C$ with liquid N_2 , and phosphorus trichloride (20.0 mL, 235 mmol) was added dropwise on top of the frozen mixture. The flask was allowed to warm to $25^\circ C$, and vigorous stirring was commenced as soon as possible. As the mixture warmed, a slight exotherm occurred, and the solution color changed from purple to brown and then yellow, and a white precipitate formed. The solution was transferred by filter cannula to a separate flask, and the solid left behind was washed with hexane (2×20 mL). The washings were added to the original filtrate, and the volatile material was removed in vacuum to afford a viscous yellow oil. The oil was dried overnight at $35^\circ C$ at 10^{-3} Torr to a yellow solid, which was used without purification in the next step. $^{31}P\{^1H\}$ NMR (162 MHz, hexane): δ 70.2 (s).

4,4'-Di-*tert*-butyl-2,2'-biphenylenedithiophosphinic acid, $\text{HS}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)$. To a solution of 3,7-di-*tert*-butyl-5-chloro-5H-dibenzophosphole (theoretical yield: 40 mmol) in toluene (50 mL) was added elemental sulfur (1.28 g, 5.0 mmol reckoned as S_8) against a counterflow of argon. The mixture was heated to reflux for 8 h. The resulting yellow solution was cooled to 25 °C and filtered to remove a small amount of yellow precipitate. The filtrate was taken to dryness in vacuum to afford a sticky yellow solid, which was triturated with absolute ethanol (60 mL). After the ethanol was removed, the solid was treated with a solution of sodium hydrosulfide hydrate (7.47 g, ca. 80.0 mmol) in $\text{H}_2\text{O}:\text{EtOH}$ (1:2 ratio with a total volume of 60 mL). The flask was purged with argon and vented with a cannula to a 2.5 M aq. NaOH solution to sequester evolved H_2S . The mixture was stirred at 25 °C for 14 h, during which time the solution color became orange and a gummy white solid precipitated. The solution was separated from the solid by vacuum filtration in air, and the filtrate was washed with hexanes (3×25 mL). The solution was transferred to a 250 Erlenmeyer flask, acidified with 2.4 M aqueous HCl (25 mL), and allowed to stir in air for 30 min. The light yellow precipitate that formed was collected by vacuum filtration and dissolved in CH_2Cl_2 (40 mL). The resulting solution was dried over MgSO_4 , and taken to dryness in vacuum to afford the product as a free-flowing, pale yellow powder. Yield: 7.48 g (52% from 4,4'-di-*tert*-butylbiphenyl). ^1H NMR (400 MHz, CDCl_3): δ 7.97 (dd, $J = 13.4, 1.7$ Hz, 2H, 3,3'-CH), 7.67 (dd, $J = 8.1, 4.2$ Hz, 2H, 6,6'-CH), 7.61 (ddd, $J = 8.1, 1.7, 1.7$ Hz, 2H, 5,5'-CH), 1.40 (s, 18H, $\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 46.4 (s). HRMS m/z (ESI $^+$). Calcd: 361.1214 $[\text{M} + \text{H}]^+$. Found: 361.1209. IR (cm^{-1}): 3047 w, 2924 s br, 2855 s, 2348 m br, 1923 w, 1809 w, 1779 w, 1689 w, 1661 w, 1599 w, 1572 w, 1462 s br, 1405 w, 1378 w, 1363 m, 1300 w, 1272 w, 1255 m, 1156 m, 1110 m, 1084 w, 1061 m, 1084 w, 1061 m, 874 w, 829 s, 794 w, 733 s, 723 s, 671 s, 603 m, 535 s.

Tetraphenylarsonium 4,4'-Di-*tert*-butyl-2,2'-biphenylenedithiophosphate,

[AsPh₄][S₂P('Bu₂C₁₂H₆)].

This compound was synthesized by treating a solution of HS₂P('Bu₂C₁₂H₆) (100.0 mg, 0.277 mmol) in aqueous NH₄OH (20.0 mL, 3.6 M) with a solution of tetraphenylarsonium chloride hydrate (182 mg, 0.417 mmol) in H₂O (5.0 mL) as described above for [PPh₄][S₂P(C₁₂H₈)]. Purification was affected by slow evaporation of a 20 mL 1:1 acetone:H₂O solution to *ca.* 5 mL, which afforded large, pale yellow needles of [AsPh₄][S₂P('Bu₂C₁₂H₆)]•0.5acetone that were suitable for X-ray diffraction. Yield: 95.2 mg (45%). Anal. Calcd. for C_{45.5}H₄₇O_{0.5}AsPS₂: C, 70.8; H, 6.14; As, 9.71; P, 4.01; S, 8.31. Found: C, 70.5; H, 6.03; As, 9.99; P, 4.12; S, 8.60%. ¹H NMR (500 MHz, d₃-MeCN): δ 7.89 – 7.84 (m, 4H, Ar-H), 7.77-7.66 (m, 18H, Ar-H), 7.63 (dd, *J* = 8.1, 3.2 Hz, 2H, 6,6'-CH), 7.42 (ddd, *J* = 8.1, 1.7, 1.7 Hz, 2H, 5,5'-CH), 1.35 (s, 18H, -C(CH₃)₃). ³¹P{¹H} NMR (162 MHz, d₃-MeCN): δ 61.8 (s). IR (cm⁻¹): 3385 br, 3048 w, 2917 s, 2856 s, 1577 w, 1460 s, 1441 s, 1378 m, 1362 m, 1312 w, 1252 m, 1187 w, 1156 w, 1113 w, 1081 m, 1023 w, 997 m, 823 m, 749 s, 727 s, 789 m, 660 s, 584 m.

Potassium 4,4'-Di-*tert*-butyl-2,2'-biphenylenedithiophosphate, K[S₂P('Bu₂C₁₂H₆)]. To a cold (0 °C) solution of 4,4'-di-*tert*-butyl-2,2'-biphenylenedithiophosphinic acid (2.15 g, 5.96 mmol) in toluene (20 mL) was added a solution of potassium hexamethyldisilazide (1.31 g, 6.57 mmol) in toluene (20 mL). The mixture, which became turbid, was stirred at 25 °C for 30 min. The white solid was collected by filtration, washed with cold (0 °C) toluene (3 × 10 mL) and hexanes (2 × 10 mL), and dried in vacuum to afford the product as a white powder. Yield: 1.94 g (82%). ¹H NMR (400 MHz, d₆-acetone): δ 7.77 (dd, *J* = 11.4, 1.8 Hz, 2H, 3,3'-CH), 7.62 (dd,

$J = 8.0, 3.2$ Hz, 2H, 6,6'-CH), 7.38 (ddd, $J = 8.0, 1.8, 1.7$ Hz, 2H, 5,5'-CH), 1.35 (s, 18H, C(CH₃)₃). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, d₆-acetone) δ : 61.6. The microanalytical data suggests the presence of the hydrate K[S₂P(^tBu₂C₁₂H₆)]•H₂O. Anal. Calcd. for C₂₀H₂₆POS₂K: C, 57.66; H, 6.29; P, 7.43; S, 15.39; K, 9.38. Found: C, 58.36; H, 6.07; P, 7.08; S, 14.51; K, 9.09 %. IR (cm⁻¹): 3387 br, 2919 s, 2856 s, 1614 w, 1459 s, 1396 w, 1363 m, 1212 m, 1202 w, 1156 m, 1111 m, 1081 w, 1059 w, 823 m, 794 w, 727 s, 647 s, 580 m.

Potassium Diphenyldithiophosphate. To KN(SiMe₃)₂ (392 mg, 1.97 mmol) dissolved in toluene was added a solution of HS₂P(C₆H₅)₂ (489 mg, 1.95 mmol) in toluene (5 mL). After 24 h, the mixture was centrifuged and the white solid was collected by filtration and washed with hexane (3 × 10 mL). The solid was dried under vacuum (10⁻³ Torr), collected as a white powder (460 mg; 82% yield), and used as KS₂P(C₆H₅)₂ for subsequent reactions.

Tetrakis(diphenyldithiophosphinato)uranium(IV), U[S₂P(C₆H₅)₂]₄. **Method A.** To a solution of U[N(SiMe₃)₂]₃ (90.0 mg, 0.125 mmol) in THF (7 mL) was added solid HS₂P(C₆H₅)₂ (94.0 mg, 0.376 mmol). The resulting mixture was stirred at ambient temperature for 3 days, and the green solution was filtered through a glass fiber filter circle. Hexanes were added to the green filtrate until a precipitate began to form. The mixture was stored at -35 °C for 2 h. The precipitate was collected on a frit by vacuum filtration, washed with hexanes (5 mL), and dried in vacuum to afford a green powder. Yield: 99.1 mg (64% based on the amount of U in the starting material). Anal. Calcd. for C₄₈H₄₀P₄S₈U: C, 46.7; H, 3.24. Found: C, 46.7; H, 3.60. ^1H NMR (300 MHz, C₆D₆): δ 12.4 (s, 16H, 2,6-CH), 9.0 (t, $J = 7.4$ Hz, 16H, 3,5-CH), 8.7 (t, $J = 7.5$ Hz, 8H, 4-CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C₆D₆): δ -581 (br s). UV/vis/NIR in THF solution

(λ_{max} , nm): 336 sh, 353 sh, 395 sh, 423 sh, 471, 534 sh, 593, 630, 663 sh, 706 sh, 772, 875 sh, 919, 1020, 1081, 1112 sh, 1237, 1252 sh. IR (cm^{-1}): 481 sh, 486, 564, 612, 647, 687, 705, 743, 1099. Single-crystals of $\text{U}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot \text{THF}$ suitable for X-ray diffraction were obtained from a THF solution of $\text{U}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ into which Et_2O was vapor diffused at ambient temperature.

Method B. In an argon filled-glovebox, a solution of UCl_4 (38.4 mg, 0.101 mmol) in THF (10 mL) was added a solution of $\text{KS}_2\text{P}(\text{C}_6\text{H}_5)_2$ (29.8 mg, 0.103 mmol) in THF (5 mL). The initially green color changed to yellow. After the mixture had been stirred for 24 h, it was centrifuged and the solution was separated from a white solid by filtration. The filtrate was taken to dryness under vacuum (10^{-3} Torr), and the resulting residue was dissolved in toluene (~5 mL). A small amount of an insoluble white precipitate was again separated by centrifugation. The toluene was removed under vacuum (10^{-3} Torr) and the resulting lime colored solid was dissolved in a minimal amount of hot THF. The solution was slowly cooled to -25°C . After 24 h, toluene was layered on the THF solution. After 1 week, the lime-colored crystals were collected. Yield: 35.0 mg, (28%).

Tetrakis(diphenyldithiophosphinato)neptunium(IV), $\text{Np}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$. Method A. To $[\text{PPh}_4]_2[\text{NpCl}_6]$ (6.6 mg, 0.006 mmol) was added a solution of $\text{KS}_2\text{P}(\text{C}_6\text{H}_5)_2$ (6.7 mg, 0.023 mmol) in THF (3 mL). The initially peach/salmon-pink mixture was stirred at ambient temperature for 2 h to give a deep red solution and a white precipitate (presumed to be KCl). The solution was filtered through a glass fiber filter circle. The deep red filtrate was concentrated in vacuum to 1.5 mL and Et_2O was vapor diffused into the solution at -35°C . After 2 days, red block-shaped crystals of $\text{Np}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4 \cdot \text{THF}$ had formed that used for the X-ray diffraction

study. ^1H NMR (300 MHz, CD_2Cl_2): δ 9.1 (s, 16H, 2,6-CH), 7.9 (s, 24H, 3,4,5-CH). $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, CD_2Cl_2): δ -701 (br s). UV/vis/NIR (THF; λ_{max} , nm): 693, 744, 759, 780 sh, 789, 821, 856, 886, 922, 976, 1024. Solid-state diffuse reflectance UV/vis/NIR (λ_{max} , nm): 693, 746, 759, 790, 820, 856, 887, 920, 978, 1021.

Method B. To solid $[\text{PPh}_4]_2[\text{NpCl}_6]$ (20.1 mg, 0.018 mmol) was added a solution of $\text{KS}_2\text{P}(\text{C}_6\text{H}_5)_2$ (20.5 mg, 0.071 mmol) in THF (3 mL). The mixture was heated at 50 °C for 30 min and then was stirred at ambient temperature for 14 h. The resulting cloudy red solution was filtered through Celite on a glass fiber filter circle. The deep red filtrate was stored at -35 °C for 4 days to afford a red solid, which was collected, washed with hexanes (5 mL), and dried in vacuum. Yield: 7.1 mg (33%).

Method C. To a solid mixture of $\text{NpCl}_4(\text{DME})_2$ (19.9 mg, 0.036 mmol) and $\text{K}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]$ (41.1 mg, 0.143 mmol) was added THF (3 mL). The resulting deep red cloudy solution was stirred at ambient temperature for 2 days and then filtered through Celite supported on a glass fiber filter circle. The filtrate was taken to dryness in vacuum, and the resulting residue was dissolved in THF (1 mL) with heating at 50 °C for 5 min. The solution was filtered through a glass fiber filter circle, layered with Et_2O , and stored at -35 °C. After one day, red crystals had deposited, which were collected and dried in vacuum. Yield: 12.6 mg (29%).

Tris(diphenyldithiophosphinato)bis(pyridine)plutonium(III), $\text{Pu}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3(\text{NC}_5\text{H}_5)_2$.
To a solution of $\text{PuI}_3(\text{NC}_5\text{H}_5)_4$ (20.6 mg, 0.022 mmol) in THF (2 mL) was added a solution of $\text{NaS}_2\text{P}(\text{C}_6\text{H}_5)_2$ formed by treating $\text{HS}_2\text{P}(\text{C}_6\text{H}_5)_2$ (16.5 mg, 0.066 mmol) with $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ (12.2

mg, 0.067 mmol) in THF (2 mL). The mixture, which quickly turned green, was stirred at ambient temperature for 6 h. The green-brown solution was taken to dryness in vacuum and the resulting green residue was dissolved in toluene (0.75 mL). The solution was filtered through a glass fiber filter circle to afford an intensely colored filtrate, into which Et₂O was slowly vapor diffused at -35 °C. After one week, a few green needles of Pu[S₂P(C₆H₅)₂]₃(NC₅H₅)₂•toluene formed that were suitable for single-crystal X-ray diffraction. Pure bulk product could not be obtained, possibly because the reaction generates several species: the ³¹P NMR spectrum of the reaction solution contains multiple broad resonances due to paramagnetic compounds.

Tetrakis(4,4'-di-*tert*-butyl-2,2'-biphenylenedithiophosphinato)uranium(IV),

U[S₂P('Bu₂C₁₂H₆)]₄. To a solution of uranium tetrachloride (12.5 mg, 0.033 mmol) in THF (3 mL) was added a solution of potassium 4,4'-di-*tert*-butyl-2,2'-dithiophosphate (52.6 mg, 0.132 mmol) in THF (5 mL). The mixture, which became turbid, was stirred at 25 °C for 22 h. The solvent was removed under reduced pressure and to the resulting residue was added toluene (2 × 5 mL). The mixture was centrifuged and the yellow solution was filtered away from a white solid. The filtrate was taken to dryness in vacuum to afford the product as a green-yellow solid. Yield: 42.3 mg (76%). Anal. Calcd. for C₈₀H₉₆P₄S₈U: C, 57.33; H, 5.77; P, 7.39; S, 15.30; U, 14.20. Found: C, 57.83; H, 5.92%. ¹H NMR (500 MHz, CDCl₃): δ:13.1 (s, 8H, 3,3'-CH), 8.49 (d, *J* = 7.6 Hz, 8H, 6,6'-CH), 8.26 (d, *J* = 7.6 Hz, 8H, 5,5'-CH), 2.55 (s, 72H, C(CH₃)₃). ³¹P{¹H} NMR (202 MHz, CDCl₃): δ -603 (br s). IR (cm⁻¹): 2955 s, 2924 s br, 1462 m br, 1377 m, 1365 w, 1255 w, 1155 w, 1110 w, 1082 w, 1060 w, 1022 w, 826 w, 794 w, 724 m, 665 w, 654 w, 614 w, 587 m. Crystallization from a mixture of THF (1.5 mL), toluene (1.5 mL), and hexane (0.5 mL) afforded green prisms of U[S₂P('Bu₂C₁₂H₆)]₄ that were suitable for X-ray diffraction.

Tetrakis(4,4'-di-*tert*-butyl-2,2'-biphenylenedithiophosphinato)neptunium(IV),

Np[S₂P(^{*t*}Bu₂C₁₂H₆)₄]. To solid NpCl₄(DME)₂ (22.6 mg, 0.040 mmol) was added a solution of potassium 4,4'-di-*tert*-butyl-2,2'-dithiophosphinate (64.8 mg, 0.162 mmol) in THF (3 mL). The deep red solution was stirred at ambient temperature for 16 h. Volatile materials were removed in vacuum, and the red residue was stirred with toluene (6 mL) at 40 °C for 10 min, causing some of the red product to dissolve although some of the red material remained undissolved. The red solution was filtered while warm through Celite supported on a glass fiber filter circle. The filtrate was concentrated in vacuum to 2.5 mL, layered with Et₂O (2.5 mL) and hexanes (13 mL), and stored at -35 °C. After eight days the red microcrystals were collected, washed with hexanes (7 mL), and dried in vacuum. Yield: 6.1 mg (9%). The unextracted red solid was dissolved in THF (4 mL) with heating at 40 °C, and the resulting solution was filtered through Celite supported on a glass fiber filter circle (to remove some undissolved white solid, presumably KCl). The deep red filtrate was layered with hexanes (6 mL) and stored at -35 °C. After three days, the red crystals that had deposited were collected, washed with hexanes (7 mL), and dried in vacuum. Yield: 33.1 mg (49%). The total combined crystalline yield of the two crops was 598%. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.2 (s, 8H, 3,3'-CH), 7.5 (d, *J* = 7.3 Hz, 8H, 6,6'-CH), 7.4 (d, *J* = 8.2 Hz, 8H, 5,5'-CH), 1.4 (s, 72H, -C(CH₃)₃). ³¹P{¹H} NMR (121 MHz, CD₂Cl₂): δ -715 (br s). UV/vis/NIR (THF; λ_{max}, nm): 480, 693, 714 sh, 745 sh, 773, 788, 814, 852, 893, 919, 971, 1025, 1284, 1322. Solid-state diffuse reflectance UV/vis/NIR (λ_{max}, nm): 482, 695, 714 sh, 747 sh, 772, 787, 815, 850, 891, 921, 971, 1016, 1024, 1283, 1323. Single crystals suitable for X-ray diffraction were obtained by adding five drops of THF to a toluene solution of the product, then

layering with hexanes (5 mL) followed by storage at -35 °C. After 6 days several large, deep-red, block shaped crystals of $\text{Np}[\text{S}_2\text{P}(\text{iBu}_2\text{C}_{12}\text{H}_6)]_4 \cdot 4\text{toluene}$ had formed.

Crystallographic Details. Single crystals of $\text{HS}_2(\text{R}_2\text{PC}_{12}\text{H}_6)$, $[\text{ZPh}_4][\text{S}_2\text{P}(\text{R}_2\text{C}_{12}\text{H}_6)]$, $\text{U}[\text{S}_2\text{P}(\text{iBu}_2\text{C}_{12}\text{H}_6)]_4$, and $\text{U}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$ were mounted in a nylon cryoloop with Paratone-N oil under argon gas flow. To ensure safe handling during the diffraction studies, crystals containing the transuranic elements Np and Pu were prepared for analyses with three appropriate layers of containment prior to single crystal X-ray diffraction studies by following modifications of the published procedures:^{41,46,48,49} Each transuranic crystal was coated in Paratone-N oil, mounted inside a 0.5 mm diameter quartz capillary, the ends sealed with capillary wax, the exterior of the capillary coated with acrylic ('Hard as Nails' nail polish) dissolved in ethyl acetate. The data were collected on a Bruker D8 diffractometer equipped with APEX II charge-coupled-device (CCD) detector. The crystal was cooled to 120(1) K by means of an American Cryoindustries low temperature device. The instrument was equipped with graphite monochromatized $\text{MoK}\alpha$ X-ray source ($\lambda = 0.71073 \text{ \AA}$), and a 0.5 mm monocapillary. A hemisphere of data was collected using ω scans, with 10-30 second frame exposures and 0.5° frame widths. Data collection and initial indexing and cell refinement were handled using APEX II software.⁵⁰ Frame integration, Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ software.⁵¹ The SADABS program was used to apply a semi-empirical absorption correction based on redundant reflections.⁵² Decay of reflection intensity was not observed as monitored via analysis of redundant frames. The structure was solved by means of direct methods and difference Fourier techniques. All hydrogen atom positions were idealized. The final refinement model included anisotropic temperature factors for all non-hydrogen atoms.

Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL and Mercury.⁵³

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Supporting Information Available. Supplementary data associated with this article, including crystallographic information (.cif) files from all compounds, a complete list of bond distances for all of the compounds reported herein, the UV-vis-NIR (solution) spectra from $U[(S_2P(C_6H_5)_2)_4]$, $Np[(S_2P(C_6H_5)_2)_4]$, and $Np[S_2P('Bu_2C_{12}H_6)]_4$. Solid phase UV-vis-NIR (solid-phase) spectra from $Np[(S_2P(C_6H_5)_2)_4]$ and $Np[(S_2P(C_6H_5)_2)_4]$ are also included as well as an IR spectrum from $U[S_2P(C_6H_5)_2]_4$. The 1H and ^{31}P NMR spectra from $KS_2P('Bu_2C_{12}H_6)$, $U[(S_2P(C_6H_5)_2)_4]$,

$\text{Np}[(\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2)]_4$, and $\text{Np}[\text{S}_2\text{P}(\text{tBu}_2\text{C}_{12}\text{H}_6)]_4$ were included. Full details of the X-ray structure determinations are available from the Cambridge Crystallographic Data Center, deposition numbers CCDC 1021660-1021664.

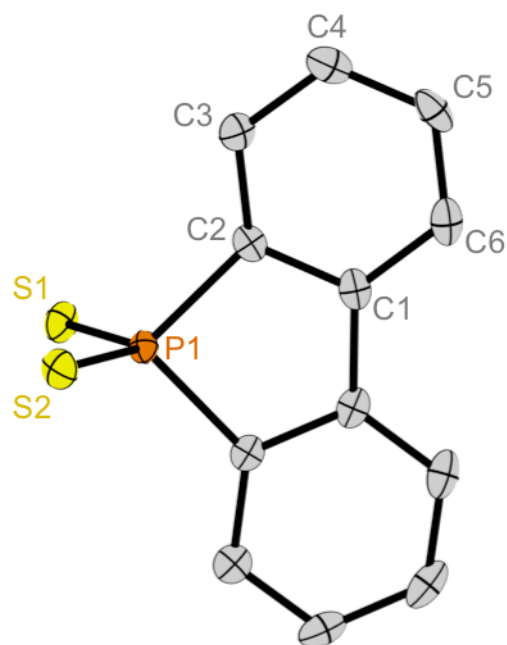


Figure 1: Molecular structure of the anion in $[\text{PPh}_4][\text{S}_2\text{P}(\text{C}_{12}\text{H}_8)]$. Thermal ellipsoids show the 50% probability density surfaces. The PPh_4^{1+} counteranion and hydrogen atoms have been omitted.

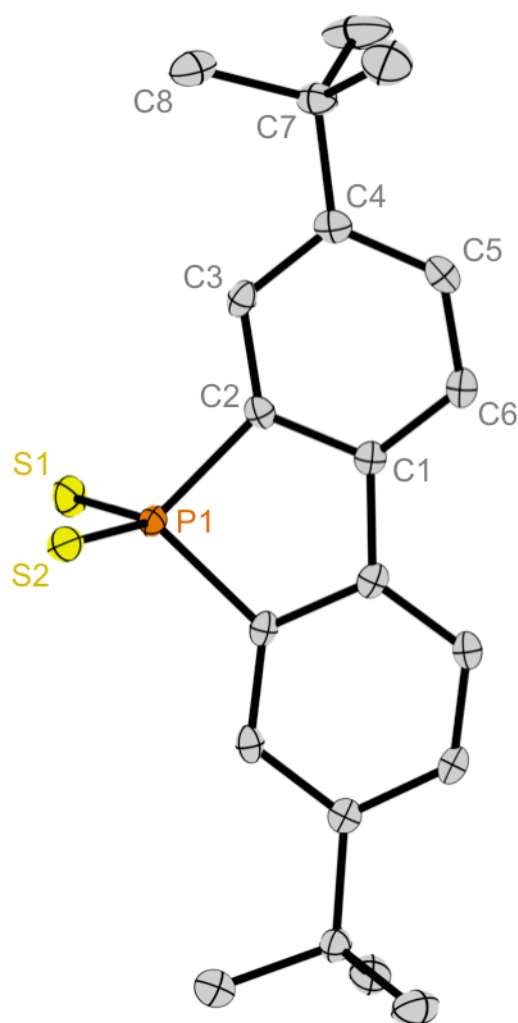


Figure 2: Molecular structure of the anion in $[\text{AsPh}_4][\text{S}_2\text{P}(\text{}^t\text{Bu}_2\text{C}_{12}\text{H}_6)]$. Thermal ellipsoids show the 50% probability density surfaces. The AsPPh_4^{1+} counteranion, solvent molecules, and hydrogen atoms have been omitted.

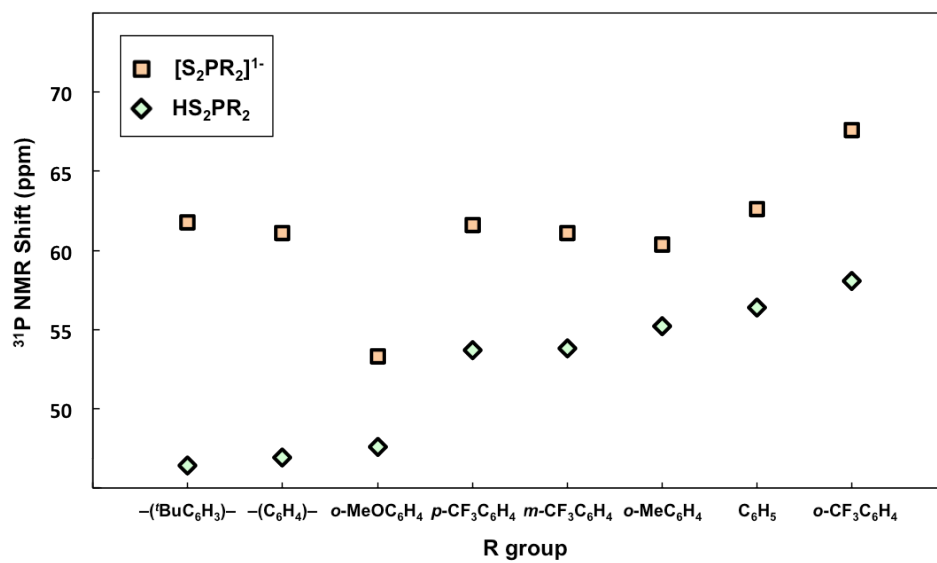


Figure 3. ^{31}P NMR shifts for the HS_2PR_2 and $[S_2PR_2]^{1-}$ compounds in $CDCl_3$ and d_3 -MeCN, respectively.

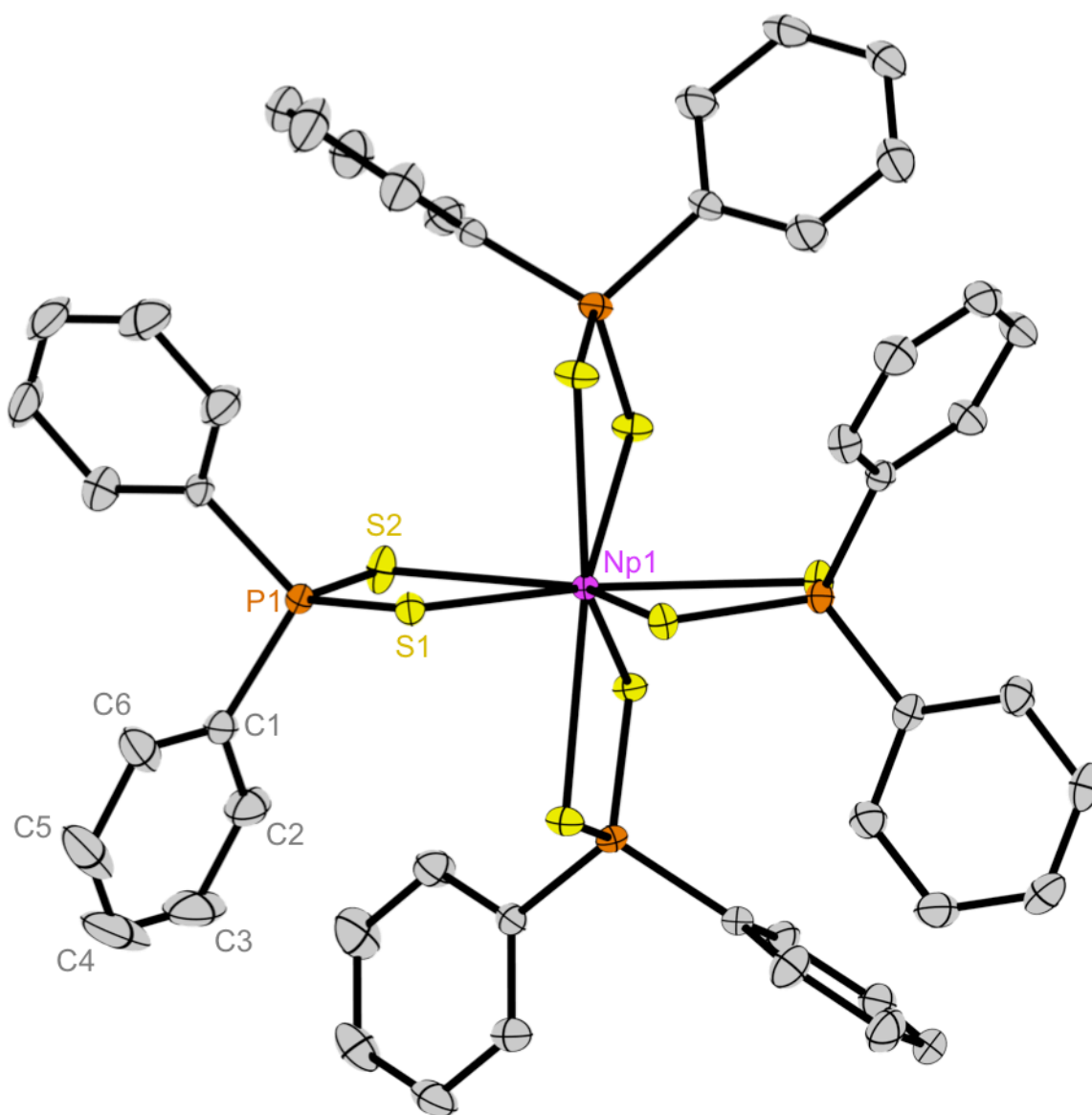


Figure 4. Molecular structure of $\text{Np}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_4$. Thermal ellipsoids show the 50% probability density surfaces. Hydrogen atoms and solvent molecules have been omitted.

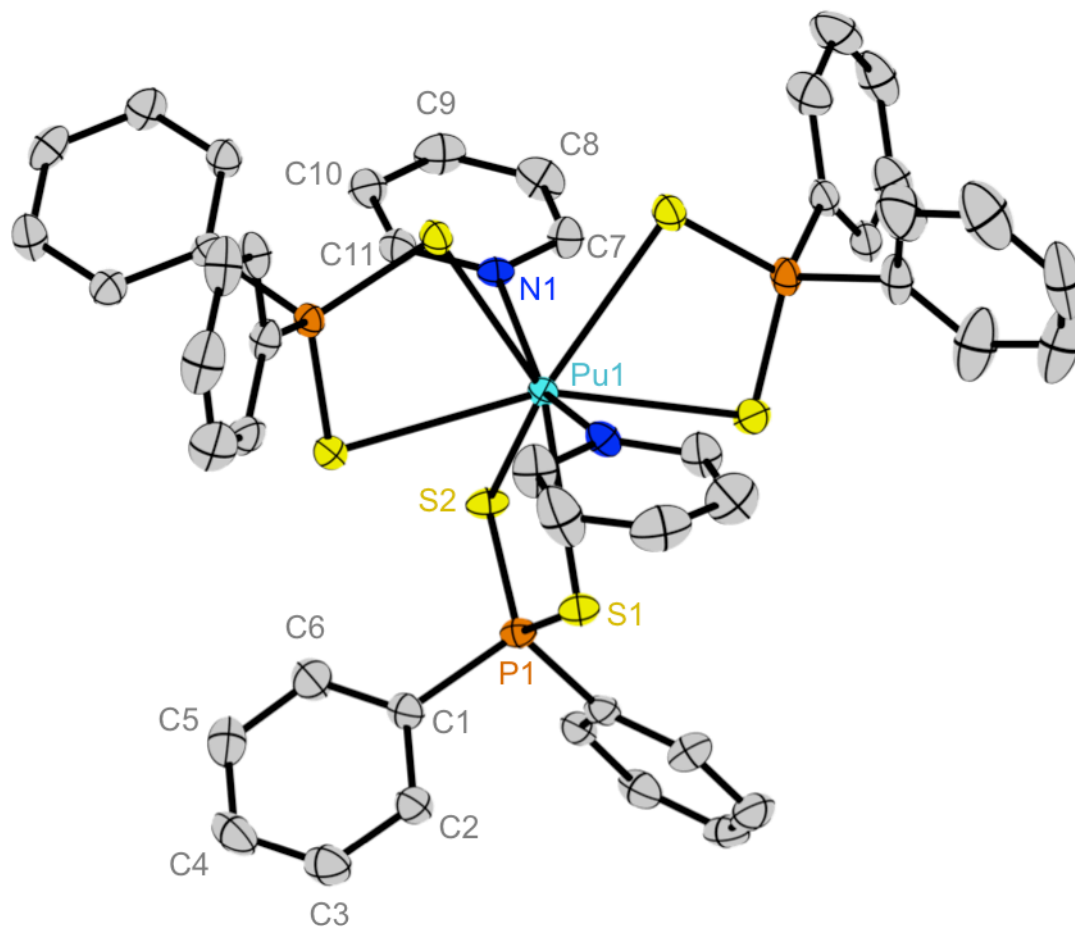


Figure 5. Molecular structure of $\text{Pu}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3(\text{NC}_6\text{H}_5)_2$. Thermal ellipsoids show the 50% probability density surfaces. Hydrogen atoms and solvent molecules have been omitted.

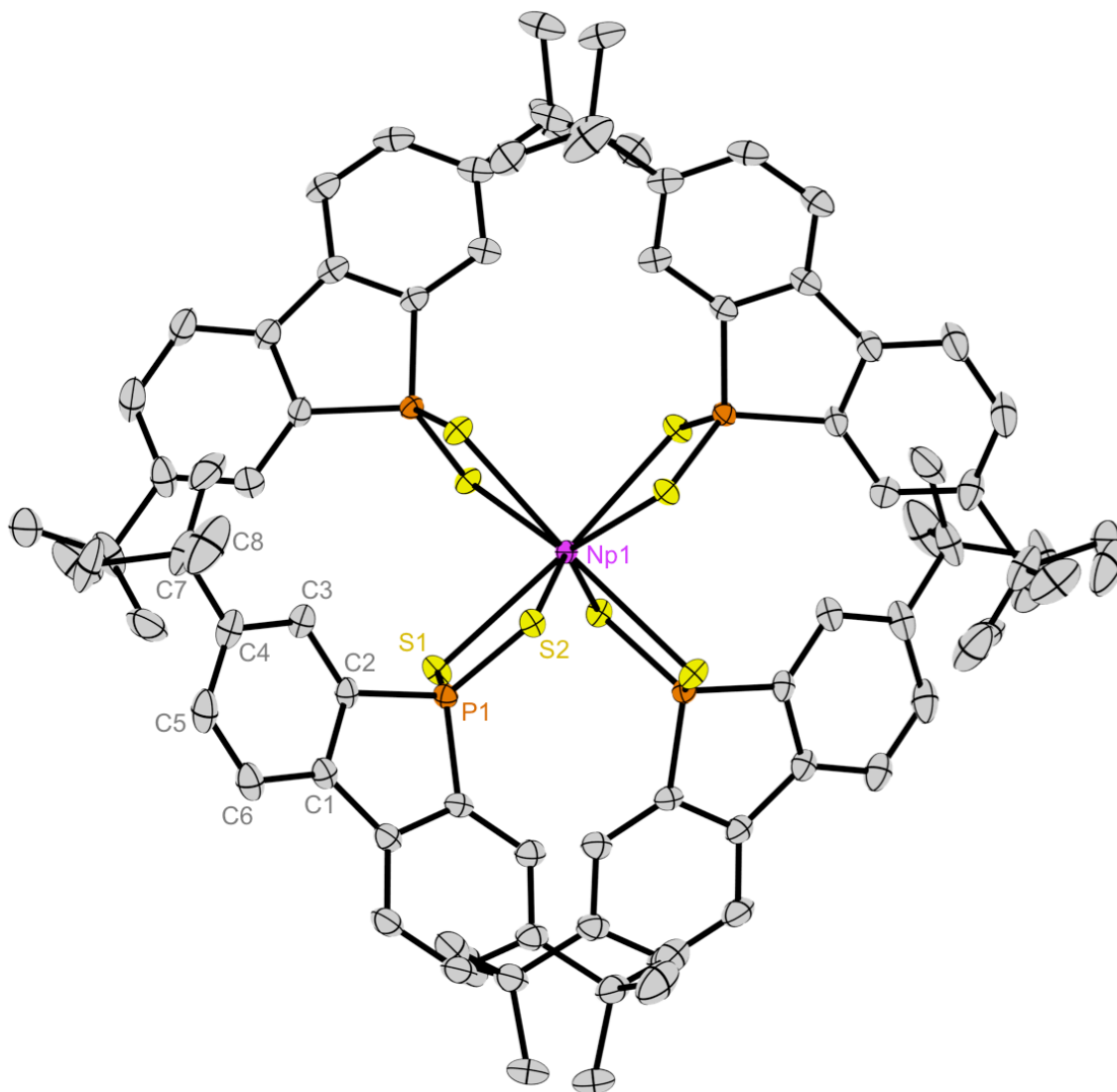


Figure 6. Molecular structure of $\text{Np}[\text{S}_2\text{P}(\text{}^t\text{Bu}_2\text{C}_6\text{H}_4)]_4$. Thermal ellipsoids show the 50% probability density surfaces. Hydrogen atoms and solvent molecules have been omitted.

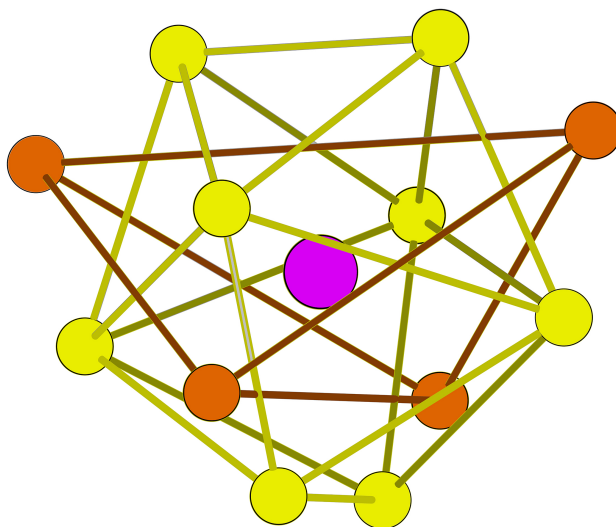


Figure 7. Ball and stick representation of $\text{Np}[\text{S}_2\text{P}(\text{}^t\text{Bu}_2\text{C}_{12}\text{H}_6)]_4$ showing the first coordination sphere of sulfur atoms (yellow distorted trigonal dodecahedron) and the second shell of phosphorus atoms (orange flattened tetrahedron) around the central Np ion (purple).

Table 1. Crystallographic data for [PPh₄][S₂P(C₁₂H₈)] and [AsPh₄][S₂P(^{*t*}Bu₂C₁₂H₆)]•0.5 acetone collected at 120(1) K.

	[PPh ₄][S ₂ P(C ₁₂ H ₈)]	[AsPh ₄][S ₂ P(^{<i>t</i>} Bu ₂ C ₁₂ H ₆)] •0.5acetone
formula	C ₃₄ H ₂₈ P ₂ S ₂	C _{45.5} H ₄₇ O _{0.5} AsPS ₂
formula wt (g mol ⁻¹)	586.69	771.84
crystal system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.616(4)	12.5652(13)
<i>b</i> (Å)	16.103(5)	13.0602(14)
<i>c</i> (Å)	16.319(5)	14.2301(15)
α (°)	90	110.587(1)
β (°)	109.164(4)	91.766(1)
γ (°)	90	114.432(1)
<i>V</i> (Å ³)	2883.3(16)	1947.3(4)
<i>Z</i>	4	2
ρ_{calcd} (g cm ⁻³)	1.351	1.316
μ (mm ⁻¹)	0.321	1.054
data/restraints/params	5494/0/361	9192/0/439
goodness-of-fit on <i>F</i> ²	1.198	1.410
<i>R</i> ₁ [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0386	0.0333
<i>wR</i> ₂ (all data)	0.0863	0.0627
largest Δρ (e•Å ⁻³)	0.364/-0.339	0.575/-0.325

Table 2. Selected bond distances and angles for [PPh₄][S₂P(C₁₂H₈)], [AsPh₄][S₂P(^tBu₂C₁₂H₈)], and other diaryldithiophosphinates.^a Error bars were given as standard deviation of the mean (at 1σ).

Cmpd	S–P (Å)	P–C (Å)	S–P–S (°)	C–P–C (°)
[PPh ₄][S ₂ P(C ₁₂ H ₈)] ^b	1.977 ± 0.002	1.821 ± 0.002	118.53(4)	90.7(1)
[AsPh ₄][S ₂ P(^t Bu ₂ C ₁₂ H ₈)] ^b	1.980 ± 0.001	1.820 ± 0.003	119.21(3)	90.75(8)
[PPh ₄][S ₂ P(C ₆ H ₅) ₂] ²⁷	1.977 ± 0.001	1.832 ± 0.001	118.13(4)	103.5(1)
[PPh ₄][S ₂ P(<i>o</i> -MeC ₆ H ₄) ₂] ²⁷	1.992 ± 0.004	1.838 ± 0.004	117.25(4)	106.9(1)
[PPh ₄][S ₂ P(<i>o</i> -MeOC ₆ H ₄) ₂] ²⁷	1.99 ± 0.01	1.836 ± 0.004	115.65(5)	104.4(1)
[PPh ₄][S ₂ P(<i>o</i> -CF ₃ C ₆ H ₄) ₂] ²⁷	1.984 ± 0.009	1.860 ± 0.006	116.46(8)	111.0(2)

^a Values given are average bond distances with standard deviations from the mean (1σ).

^bThis work.

Table 3. Crystallographic data for actinide dithiophosphinate complexes.

	U[S₂P('Bu₂C₁₂H₆)]₄ •toluene	Np[S₂P('Bu₂C₁₂H₆)]₄ •4toluene	U[S₂P(C₆H₅)₂]₄ •THF	Np[S₂P(C₆H₅)₂]₄ •THF	Pu[S₂P(C₆H₅)₂]₃ (NC₅H₅)₂•toluene
formula	C ₈₇ H ₁₀₄ P ₄ S ₈ U	C ₁₀₈ H ₁₂₈ NpP ₄ S ₈	C ₅₂ H ₄₈ OP ₄ S ₈ U	C ₅₂ H ₄₈ NpOP ₄ S ₈	C ₅₃ H ₄₈ N ₂ P ₃ PuS ₆
formula wt (g mol ⁻¹)	1768.09	2043.46	1307.29	1306.26	1237.29
crystal system	orthorhombic	monoclinic	triclinic	Triclinic	triclinic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	17.760(3)	22.8029(17)	10.9621(7)	10.9835(9)	11.770(2)
<i>b</i> (Å)	19.279(4)	20.2642(15)	13.3551(9)	13.3013(10)	14.808(3)
<i>c</i> (Å)	25.446(5)	23.9268(17)	18.5207(12)	18.4912(14)	16.972(3)
α (°)	90	90	94.845(1)	94.945(1)	79.148(2)
β (°)	90	110.020(1)	95.092(1)	95.113(1)	70.433(2)
γ (°)	90	90	96.650(1)	96.364(1)	69.036(2)
<i>V</i> (Å ³)	8713(3)	10388.1(13)	2670.2(3)	2661.5(4)	2594.8(8)
<i>Z</i>	4	4	2	2	2
ρ_{calcd} (g cm ⁻³)	1.348	1.307	1.626	1.63	1.587
μ (mm ⁻¹)	2.17	1.268	3.51	2.424	1.642
data/restraints/params	18631/0/926	22227/6/457	10022/0/595	12585/0/595	11790/42/575
goodness-of-fit on <i>F</i> ²	0.831	1.722	1.000	1.100	0.933
<i>R</i> ₁ [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.0288	0.0508	0.0333	0.0223	0.0351
<i>wR</i> ₂ (all data)	0.0482	0.1457	0.0913	0.048	0.0674
largest Δρ (e•Å ⁻³)	0.595/-0.976	3.787/-3.027	3.587/-1.760	1.141/-0.613	1.154/-1.059

Table 4. Selected average bond distances and average angles for actinide dithiophosphinate complexes. Error bars were given as standard deviation of the mean (at 1σ).

	U[S₂P(ⁱBu₂C₁₂H₆)]₄ •toluene	Np[S₂P(ⁱBu₂C₁₂H₆)]₄ •4toluene	U[S₂P(C₆H₅)₂]₄ •THF	Np[S₂P(C₆H₅)₂]₄ •THF	Pu[S₂P(C₆H₅)₂]₃ (NC₅H₅)₂•toluene
M–S (Å)	2.85 ± 0.02	2.83 ± 0.01	2.85 ± 0.03	2.82 ± 0.03	2.93 ± 0.02
M–N (Å)	NA	NA	NA	NA	2.62 ± 0.01
P–S (Å)	2.001 ± 0.007	2.003 ± 0.006	2.014 ± 0.006	2.009 ± 0.003	1.997 ± 0.006
P–C (Å)	1.800 ± 0.007	1.794 ± 0.003	1.814 ± 0.005	1.809 ± 0.003	1.816 ± 0.006
C–C_{tether} (Å)	1.477 ± 0.005	1.477 ± 0.003	NA	NA	NA
C–C_{aryl} (Å)	1.39 ± 0.01	1.40 ± 0.01	1.39 ± 0.01	1.38 ± 0.01	1.38 ± 0.01
S–P–S (°)	109.4 ± 0.9	109.8 ± 0.1	109.4 ± 0.1	109.0 ± 0.1	111.8 ± 0.6
C–P–C (°)	92.4 ± 0.2	92.5 ± 0.3	105.2 ± 1.6	105.2 ± 1.3	104.1 ± 0.9
S–M–S (°)	70.0 ± 0.7	70.8 ± 0.1	70.6 ± 0.2	70.8 ± 0.1	68.7 ± 0.6

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